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THE CRYSTAL STRUCTURE OF DECAPHENYL-1-OXACYCLOHEXASILANE·0.5 C_6H_6 SOLVATE

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Summary

The crystal structure of decaphenyl-1-oxacyclohexasilane·0.5 C_6H_6 solvate is reported. This is the first crystal structure determination for an example of the little known class of polycyclohexasilanes containing a heteroatom. The conformation of the molecule is close to the 1,4-boat form with the oxygen and a silicon atom on the same side of the least-squares plane of the remaining atoms. Two types of Si–Si bonds were found, related by the mirror-symmetry of the ring, with mean bond lengths of 2.391(1) [(O)–Si–Si–(Si)] and 2.373(2) Å [(Si)–Si–Si–(Si)]. The Si–O–Si valence angle is 146.0(5)° and the mean Si–C bond distance 1.877(3) Å.

Introduction

Decaphenyl-1-oxacyclohexasilane, a new example of the little known class of six-membered cyclopolysilanes with one heteroatom, was recently prepared [1].

The structures of all known six-membered isocyclic silanes have been determined, but no structural information is available on heterocyclic compounds. The structures of the isocyclic systems Si_6Ph_{12} [2] and Si_6Me_{12} [3] were found to involve cyclohexane-like chair-conformations. An electron diffraction study on Si_6H_{12} [4] indicated that there was only a very small energy difference between possible (chair-, boat- and twist-) conformations, so that there is ready interconversion and a mixture of conformational species is present at the experimental temperature.

The exchange of one silicon atom for oxygen may result in a predominant conformation and the bulky phenyl groups may also have important influence on the structure. An X-ray structural analysis of the title compound was therefore carried out to reveal the conformational and structural features of this heterocyclic compound.

(Continued on p. 170)

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TABLE 1

FINAL ATOMIC COORDINATES ($\times 10^4$) FOR THE NON-HYDROGEN ATOMS. B_{eq} is defined as $B_{eq} = 4(b_{11}b_{22}b_{33}/a^{*2}b^{*2}c^{*2})^{1/3}$ (Å^2). C(1s), C(2s) and C(3s) atoms are isotropic

	x/a	y/b	z/c	B_{eq}		x/a	y/b	z/c	B_{eq}
Si(1)	7394(1)	−548(2)	4637(1)	3.16(4)	C(30)	7061(4)	2054(6)	1851(3)	4.2(2)
Si(2)	6924(1)	907(2)	4058(1)	2.97(4)	C(31)	8321(3)	1576(6)	3434(3)	3.1(1)
Si(3)	7414(1)	1076(2)	3113(1)	2.89(4)	C(32)	8529(4)	2451(6)	3228(4)	4.8(2)
Si(4)	7451(1)	−472(2)	2608(1)	2.93(4)	C(33)	9210(4)	2788(7)	3450(4)	6.6(2)
Si(5)	7955(1)	−1572(2)	3500(1)	3.24(4)	C(34)	9694(4)	2248(7)	3871(4)	5.8(2)
O	7903(2)	−1081(3)	4217(2)	3.45(9)	C(35)	9508(4)	1369(7)	4094(4)	5.3(2)
C(1)	7930(3)	−338(5)	5510(3)	3.3(1)	C(36)	8827(3)	1027(6)	3874(3)	4.4(2)
C(2)	7681(4)	246(7)	5950(3)	5.2(2)	C(37)	6533(3)	−752(5)	2137(3)	3.1(1)
C(3)	8023(4)	357(7)	6621(4)	6.4(2)	C(38)	6199(4)	−177(6)	1603(3)	4.9(2)
C(4)	8636(4)	−124(8)	6860(3)	6.1(2)	C(39)	5519(4)	−286(6)	1263(4)	6.2(2)
C(5)	8903(4)	−700(8)	6449(4)	7.1(2)	C(40)	5121(4)	−988(7)	1448(4)	5.7(2)
C(6)	8550(4)	−803(7)	5770(3)	5.1(2)	C(41)	5402(3)	−1606(6)	1969(4)	5.4(2)
C(7)	6686(3)	−1412(5)	4711(3)	3.4(1)	C(42)	6111(3)	−1484(5)	2322(3)	4.6(2)
C(8)	6699(3)	−1934(6)	5298(4)	4.8(2)	C(43)	8023(3)	−499(5)	1993(3)	3.1(1)
C(9)	6209(4)	−2633(7)	5343(4)	7.1(2)	C(44)	7886(3)	−1168(6)	1473(3)	4.7(2)
C(10)	5698(4)	−2834(7)	4779(5)	7.4(2)	C(45)	8332(4)	−1264(6)	1038(3)	5.7(2)

C(11)	5650(4)	−2341(7)	4190(4)	6.5(2)	C(46)	8921(4)	−694(6)	1143(3)	6.6(2)
C(12)	6134(4)	−1630(6)	4155(3)	4.9(2)	C(47)	9066(4)	−35(6)	1651(4)	6.2(2)
C(13)	5945(4)	828(7)	3823(4)	3.0(2)	C(48)	8620(3)	59(6)	2078(3)	4.8(2)
C(14)	5592(5)	845(8)	4341(4)	4.2(2)	C(49)	8911(3)	−1722(5)	3523(3)	3.7(1)
C(15)	4868(9)	810(9)	4203(5)	6.0(3)	C(50)	9103(4)	−2173(6)	2991(3)	5.1(2)
C(16)	4499(5)	759(9)	3534(6)	4.6(3)	C(51)	9796(3)	−2294(7)	2985(3)	6.9(2)
C(17)	4802(5)	722(9)	3015(5)	5.1(3)	C(52)	10310(4)	−1949(7)	3506(4)	7.2(2)
C(18)	5527(5)	756(7)	3169(5)	3.5(2)	C(53)	10132(4)	−1502(7)	4034(4)	6.4(2)
C(19)	7149(4)	2053(7)	4582(4)	2.9(2)	C(54)	9443(3)	−1416(6)	4038(4)	5.1(2)
C(20)	7832(4)	2241(9)	4971(4)	3.6(2)	C(55)	7589(3)	−2831(5)	3452(3)	3.4(1)
C(21)	7992(5)	3096(9)	5319(5)	4.7(3)	C(56)	7398(4)	−3370(6)	2863(3)	5.2(2)
C(22)	7486(6)	3784(8)	5295(5)	4.8(3)	C(57)	7183(4)	−4338(6)	2868(4)	6.5(2)
C(23)	6823(5)	3629(8)	4933(5)	4.4(2)	C(58)	7172(5)	−4768(6)	3470(5)	7.3(3)
C(24)	6664(5)	2786(7)	4574(4)	3.4(2)	C(59)	7322(5)	−4249(7)	4033(4)	8.7(3)
C(25)	6930(4)	1994(7)	2491(4)	2.6(2)	C(60)	7537(4)	−3285(6)	4036(4)	5.9(3)
C(26)	6438(4)	2622(6)	2633(3)	3.7(2)	C(1*s*)	9740(5)	862(8)	68(5)	7.9(3)
C(27)	6099(4)	3288(6)	2170(4)	5.2(2)	C(2*s*)	10373(5)	673(8)	465(5)	8.9(3)
C(28)	6229(4)	3343(6)	1533(3)	4.6(2)	C(3*s*)	9317(6)	302(9)	−405(5)	10.4(3)
C(29)	6715(4)	2714(6)	1382(3)	4.3(2)					

Experimental

The title compound was prepared by the hydrolysis of 1,5-dichloro-decaphenylpentasilane and elimination of 1 mole of water from the resulting stable α,ω-diol in vacuo [1]. The product was recrystallized from a mixture of benzene and petroleum ether to give material of m.p. 168–170°C.

Crystal data

$C_{60}H_{50}Si_5O \cdot 0.5\ C_6H_6$, Fwt. 966.6, a 19.734(6), b 13.730(7), c 20.441(8) Å, β 104.12(5)° (from single crystal diffractometry), V 5371.1(7.2) Å^3, $Z = 4$, μ(Mo-K_α, $\lambda = 0.71073$ Å) 1.76 cm^{-1}, D_x 1.195 Mg m^{-3}, space group $P2_1/c$.

Intensity data, the determination and refinement of the structure

9412 independent intensities were recorded on an Enraf-Nonius CAD-4 four-circle computer controlled single crystal diffractometer with graphite monochromated Mo-K_α-radiation. The approximate size of the crystal was 0.4 × 0.3 × 0.2 mm.

The positions of the six atoms forming the oxacyclohexasilane ring were determined by the MULTAN program [5] using 313 normalized structure factors

TABLE 2

CALCULATED HYDROGEN ATOMIC COORDINATES ($\times 10^3$). Isotropic temperature factors for the hydrogen atoms are derived from the B_{eq} values of the carbon atoms to which they are bonded. $B_H = B_{eq} + 1$ (Å^2)

	x/a	y/b	z/c		x/a	y/b	z/c
H(2)	723	62	576	H(32)	818	286	291
H(3)	782	80	691	H(33)	934	344	329
H(4)	890	−3	733	H(34)	1019	249	402
H(5)	934	−111	661	H(35)	986	97	442
H(6)	874	−124	546	H(36)	870	38	403
H(8)	709	−181	570	H(38)	647	35	145
H(9)	624	−298	577	H(39)	531	15	88
H(10)	534	−333	479	H(40)	462	−106	120
H(11)	528	−250	378	H(41)	511	−214	210
H(12)	609	−126	373	H(42)	632	−192	271
H(14)	587	88	482	H(44)	746	−159	141
H(15)	462	82	458	H(45)	822	−174	66
H(16)	398	75	343	H(46)	925	−77	84
H(17)	452	67	254	H(47)	949	38	172
H(18)	576	73	279	H(48)	873	54	245
H(20)	820	174	499	H(50)	873	−242	260
H(21)	848	322	559	H(51)	992	−263	260
H(22)	761	441	555	H(52)	1081	−202	350
H(23)	645	413	493	H(53)	1050	−124	442
H(24)	618	269	429	H(54)	932	−111	444
H(26)	633	259	308	H(56)	742	−306	243
H(27)	575	374	229	H(57)	704	−471	244
H(28)	598	382	119	H(58)	705	−547	348
H(29)	682	274	93	H(59)	728	−456	446
H(30)	741	161	173	H(60)	766	−292	447

($E \geq 2.10$), $R = 0.45$. The remaining carbon atoms were located in subsequent Fourier maps ($R = 0.21$).

2440 reflexions were used in anisotropic least-squares refinement of the non-hydrogen atoms with hydrogen atoms included in assumed positions ($R = 0.12$). At this stage a difference map was computed which revealed 3 strong peaks (3.0–4.0 e Å^{-3}) at bonded distance from each-other around the inversion center at (1,1/2,0) forming a hexagon with their symmetry-generated counter-parts. Three carbon atoms of the benzene solvent molecule were then included in the subsequent calculations with isotropic temperature factors. Other heavy atoms were anisotropically refined using 4154 reflexions $[F_o^2 \geqq 2\sigma(F_o^2)]$.

The weighting factor used was $w = [\sigma^2(F_o) + 0.25(0.01F_o)^2]^{-1}$. The final conventional and weighted R factors were R 0.078 and R_w 0.069. Final atomic parameters are listed in Tables 1 and 2.

All calculations were performed on a PDP 11/34 (64 K) minicomputer using the E.N. SDP program package and local programs. Tables of structure factors and anisotropic temperature factors may be obtained from the authors.

Discussion

The molecular diagram is shown in Fig. 1, the relevant bond distances and angles are reported in Table 3.

The Si$_5$O oxacyclohexasilane ring is puckered. The total puckering amplitude Q

TABLE 3

RELEVANT BOND LENGTHS (Å) AND ANGLES (°)

Si(1)-O	1.644(4)	Si(3)-C(25)	1.877(8)
Si(1)-Si(2)	2.391(3)	Si(3)-C(31)	1.880(6)
Si(1)-C(1)	1.862(5)	Si(4)-Si(5)	2.390(3)
Si(1)-C(7)	1.868(6)	Si(4)-C(37)	1.872(6)
Si(2)-Si(3)	2.375(2)	Si(4)-C(43)	1.884(5)
Si(2)-C(13)	1.876(8)	Si(5)-O	1.638(4)
Si(2)-C(19)	1.894(9)	Si(5)-C(49)	1.888(6)
Si(3)-Si(4)	2.371(3)	Si(5)-C(55)	1.866(7)
Si(2)-Si(1)-O	109.1(3)	Si(4)-Si(3)-C(31)	110.6(4)
Si(2)-Si(1)-C(1)	113.9(4)	C(25)-Si(3)-C(31)	106.0(4)
Si(2)-Si(1)-C(7)	111.3(4)	Si(3)-Si(4)-Si(5)	106.6(2)
O-Si(1)-C(1)	107.1(4)	Si(3)-Si(4)-C(37)	106.2(3)
O-Si(1)-C(7)	109.0(4)	Si(3)-Si(4)-C(43)	113.3(3)
C(1)-Si(1)-C(7)	106.4(5)	Si(5)-Si(4)-C(37)	115.6(4)
Si(1)-Si(2)-Si(3)	107.3(2)	Si(5)-Si(4)-C(43)	106.9(3)
Si(1)-Si(2)-C(13)	109.3(5)	C(37)-Si(4)-C(43)	108.4(5)
Si(1)-Si(2)-C(19)	113.9(4)	Si(4)-Si(5)-O	108.5(3)
Si(3)-Si(2)-C(13)	113.3(5)	Si(4)-Si(5)-C(49)	108.4(3)
Si(3)-Si(2)-C(19)	107.0(4)	Si(4)-Si(5)-C(55)	117.5(4)
C(13)-Si(2)-C(19)	106.1(6)	O-Si(5)-C(49)	107.6(4)
Si(2)-Si(3)-Si(4)	109.2(2)	O-Si(5)-C(55)	108.7(4)
Si(2)-Si(3)-C(25)	112.1(5)	C(49)-Si(5)-C(55)	105.8(5)
Si(2)-Si(3)-C(31)	107.1(4)	Si(1)-O-Si(5)	146.0(5)
Si(4)-Si(3)-C(25)	111.8(5)		

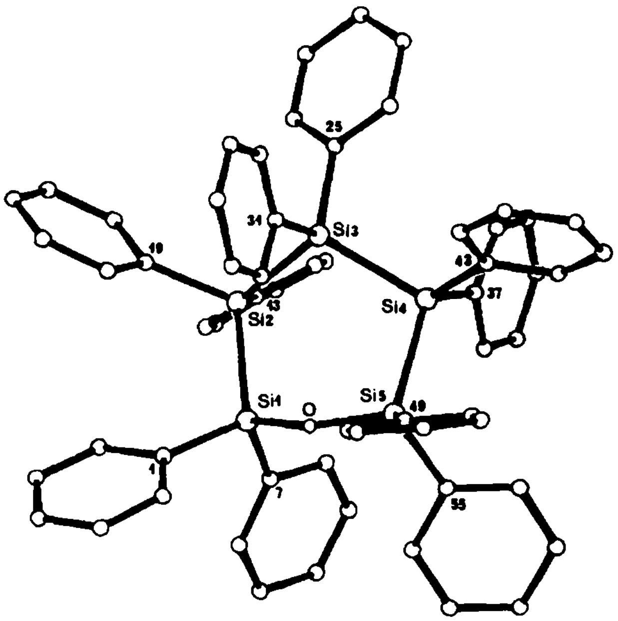

Fig. 1. A perspective view of the molecule with the numbering of atoms. Bridgehead carbon atoms are indicated with bare numbers. Hydrogen atoms are omitted for clarity.

[6] is 0.779 Å with $\phi = 12.41$ and $\theta = 110.1°$. The ring conformation is close to the ^{1,4}B (boat) form according to Boeyens' [7] notation. The pure ^{1,4}B form would require ϕ and torsion angles I and IV (cf Table 4) to be exactly zero. The mirror plane passing through the oxygen and Si(3) silicon atoms has an asymmetry parameter [5] of 11.3°. The conformation of the Si_5O ring is depicted in Fig. 2. The O and Si(3) atoms are on the same side of the least-squares plane ($-0.8391X - 0.4867Y - 0.2428Z + 12.2563 = 0$) of the remaining four silicon atoms, which do not themselves define an exact plane (the mean deviation from the plane is 0.08(1) Å). The distance of O and Si(3) from this plane is −0.374(4) and −0.935(2) Å.

A wealth of structural data on the organic analogues (pyranose rings) of the Si_5O ring is available. A connectivity search of the Cambridge Crystallographic Data files retrieved 194 entries with 243 pyranose rings reported with error-free coordinates. These data were subjected to further conformational calculations. Examples of 1,4-boat conformations with the oxygen atom in the mirror plane were specifically sought. All the rings with three exceptions [9,10] have atom (1) (oxygen) and atom (4) on different sides of the plane of the remaining four atoms (the signs of the

TABLE 4

ENDOCYCLIC TORSION ANGLES (°)

I	O-Si(1)-Si(2)-Si(3)	2.6(3)	IV	Si(3)-Si(4)-Si(5)-O	18.1(3)
II	Si(1)-Si(2)-Si(3)-Si(4)	40.9(2)	V	Si(4)-Si(5)-O-Si(1)	50.3(3)
III	Si(2)-Si(3)-Si(4)-Si(5)	−48.4(2)	VI	Si(5)-O-Si(1)-Si(2)	−59.6(7)

normal distances from the plane are different). The chair conformation predominates, and the exceptions [9,10] involve twist-boat conformation.

The conformation of the cyclopolysilane rings is expected to be similar to that of the carbon analogues (e.g. [11]). The observed conformation of the Si_5O ring in the title compound is probably caused by the presence of the bulky phenyl substituents.

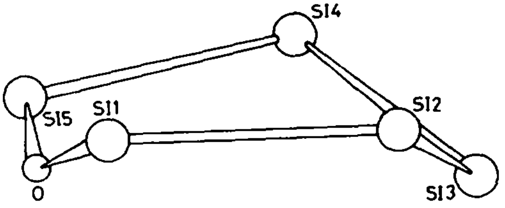

Fig. 2. A side view of the Si_5O ring.

The arrangement of the phenyl rings around the Si_5O core of the molecule has similar features to those in octaphenylcyclotetrasilane [9] and decaphenylcyclopentasilane [10]. The bridgehead carbon atoms of the phenyl groups are positioned at different distances below and above the plane formed by the silicon atom to which they are bonded and the two neighbouring atoms (either silicon or oxygen); the mean distances of the bridgehead atoms from these planes are ± 1.45(2) and ± 1.55(2) Å. The phenyl groups belonging to the Si(2)–Si(1)–O–Si(5) part of the Si_5O ring are at sequentially alternating heights while those attached to the Si(2)–Si(3)–Si(4)–Si(5) part are "in phase" (Fig. 3). The imperfect boat conformation may be attributed to the asymmetry of the arrangement of the substituents presumably governed by the need to minimize intramolecular close contacts. The

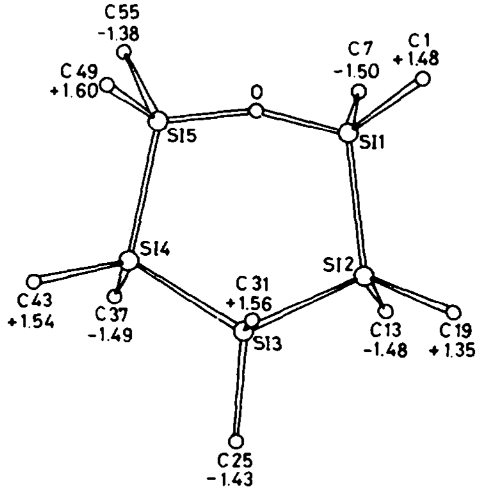

Fig. 3. A view of the six-membered ring with the bridgehead carbon atoms of the phenyl groups. The distances (Å) of these atoms from the plane formed by the silicon atoms to which they are bonded and the two neighbouring atoms are also given.

mean dihedral angle formed by two phenyl groups attached to the same silicon atom is 75(4)°.

Two types of Si–Si bond distances are found and their distribution closely fits the approximate mirror-symmetry of the Si_5O ring. One type is adjacent to the Si–O bonds, and has a mean length of 2.391(1) Å (Si(1)–Si(2) and Si(4)–Si(5) bonds), and the other type is wedged between silicon atoms and has a mean length of 2.373(2) Å (Si(2)–Si(3) and Si(3)–Si(4) bonds). The wide valence angle of 146.0(5)° at the oxygen atom typical of siloxanes is retained in the ring structure.

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